Journal of Chromatography, 640 (1993) 425–431
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2668

Separation of metal ions by capillary electrophoresis

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ABSTRACT

A number of experimental parameters have been optimized for the separation of 26 metal ions, including alkali, alkaline earth, transition and lanthanide metal ions. Experimental parameters that were evaluated included nature of indirect-detection reagent, pH of electrolyte, concentration of complexing agent and nature of the surface of the capillary; unbonded and C_1 and C_{18} bonded phases were studied. In addition the effect of internal diameter on linearity and signal-to-noise ratio was examined, and separation efficiency was determined for a variety of experimental conditions. Detecton limits (signal-to-noise ratio = 3) were *ca.* 1 μg/ml for the lanthanides, *ca.* 0.6 μg/ml for transition and alkaline earth ions and *ca.* 0.1–0.8 μg/ml for alkali metal ions. The average relative standard deviations of were 3.7, 5.1 and 2.5% on unbonded, C_1 and C_{18} capillaries, respectively. Whereas conventional regression analysis suggested that the calibration curves were linear over the range of $1 \cdot 10^{-5}$ to $4 \cdot 10^{-4}$ mol/l, sensitivity plots showed that the results were actually linear to within 6% only over the range of $2.5 \cdot 10^{-5}$ to $4 \cdot 10^{-4}$ mol/l.

INTRODUCTION

Metal ions are important in a variety of research and industrial areas, and for many analysis situations ion chromatography (IC) has been used to determine these ions [1–5]. Recently, capillary electrophoresis (CE) has attracted considerably attention as an alternative to traditional chromatographic techniques, particulary in the biological sciences. To date relatively few papers have been published on the CE separation of metal ions [6–21]. Metal ions that have been separated include the alkali, alkaline earth, transition and lanthanide ions. The high resolution of CE suggests that it should be possible to simultaneously separate a mixture containing metal ions from all of these classes, but to do so would require optimization of a number of experimental parameters. In this paper the simultaneous separation 26 metal ions including 3 alkaline, 3 alkaline earth, 6 transition metal ions and 14 lanthanides has been optimized in terms of indirect-detection reagent, pH, concentration of complexing agent and nature of the surface of the capillary. In addition the effect of internal diameter on linearity and signal-to-noise ratios was examined, and separation efficiency was determined for a variety of experimental conditions.

EXPERIMENTAL

Apparatus and electrophoresis

A Waters Quanta 4000 CE system (Millipore Waters, Milford, MA, USA) equipped with a high-voltage power supply (30 kV) was used for all separations; a positive power supply was used except when cetyltrimethylammonium chloride (CTAC) was used. Polyimide-coated (outer surface) fused-silica capillaries, 50–60 cm in length (350 μm O.D.) with inside diameters of 75, 50 and 25 μm were obtained from Polymicro Technology (Phoenix, AZ, USA). The window of the on-column detector cell was created by burning a small section (*ca.* 0.5 cm) of the polyimide coating off with a match, and excess residue was then wiped off with methanol or acetone. The unbonded capillaries were washed with 0.1 mol/l HCl for 1 h, rinsed with water, then equilibrated overnight with the electrolyte. The bonded-phase capillaries were prepared as described previously [19]. The sample was injected hy-

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0021-9673/93/$06.00

drostatically with the capillary inlet placed 9.8 cm above the capillary outlet for 1 s per each 10 cm length of capillary, sample volumes were in the range of 7 nl for a 60 cm × 75 μm capillary. The electrolyte was monitored at 214 nm, and the electric field was 500 V/cm. The electropherogram was recorded and evaluated on a PC computer with a Waters SIM interface and Waters Baseline 820 software.

Chemicals

All solutions were prepared from distilled, deionized and redistilled water (Mega-Pure system, MP-6A and D2, Corning, New York, NY, USA). The electrolyte buffer was prepared by dissolving the desired amount of an indirect-detection reagent and α-hydroxyisobutyric acid (HIBA) in water; the pH was adjusted with acetic acid [British Drug Houses (BDH), Toronto, Canada] to the desired value. The pH was measured with a combination glass electrode calibrated with pH 4.00 ± 0.02 and 7.00 ± 0.02 buffers (hydrion dry buffers, Aldrich, Milwaukee, WI, USA). The electrolytes containing surfactants were obtained by diluting a 0.01 mol/kg surfactant stock solution with the buffer. The concentration of all surfactants was below the critical micelle concentration. Triton X-100 (TX-100, Aldrich) was used without further purification. CTAC [Aldrich, 25% (w/w) aqueous solution] was freeze-dried, recrystallized twice in acetone–ethanol (1:9, v/v) and dried in a vacuum oven at 60°C overnight. All electrolyte solutions were filtered through a 0.2-μm nylon-66 membrane syringe filters (Cole-Parmer Instrument, Chicago, IL, USA) prior to use. The N,N-dimethylbenzylamine (DBA), benzylamine and naphthenemethylamine (all from Aldrich) were purified by distillation under vacuum. Benzyltrimethylammonium chloride (Aldrich) was recrystallized from methanol–diethyl ether, and N-1-naphthylethylenediamine dihydrochloride (Eastman, Rochester, NY, USA) was recrystallized from water. Creatinine (Sigma, Louis, MO, USA) was used without further purification.

Lanthanide samples were obtained from Alfa (Danvers, MA, USA) as nitrate salts (Dy, Eu, Gd, Ce) chloride salts (La, Pr, Yb) and oxides (Nd, Sm, Lu, Tm, Ho, Eu, Tb). Nitrate and chloride salts were dissolved directly in water. Oxides were dissolved in an excess of 0.5 mol/l nitric acid, evaporated to dryness and redissolved in water to form a 0.01 mol/l stock solution. The stock solutions of other metal ions were prepared from KCl, NaCl, LiCl, $MnCl_2$, $ZnCl_2$, $FeCl_2$, $BaCl_2$, $CoCl_2$ (all from BDH), $Ni(NO_3)_2$ (Fisher Scientific), $Mg(NO_3)_2$ (BDH) and $Ca(NO_3)_2$ (BDH). All stock solutions were filtered through 0.2-μm nylon-66 membrane syringe filters, and samples were prepared by dilution of the stock solution to 2 ml in the electrolyte.

RESULTS AND DISCUSSIONS

Indirect detection reagent

UV absorption is used widely to monitor compounds in CE, but most metal ions do not exhibit appreciable absorption in this range. Therefore indirect detection, where the analyte ions replace a UV-absorbing ion of the same charge (electrolyte coion) [22], has become a commonly used technique to detect metal ions as negative peaks. The equivalents of replaced coion is closely related to the equivalents of analyte injected, and thus the higher the molar absorbance of the coion, the lower the detection limit. The background absorption should be adjusted to be close to maximum value for the linear range of the detector in order to give the maximum linear calibration range. With DBA the range of linearity was below 0.05 A.U. on 75-μm and 50-μm capillaries. Consequently, the concentration of the different indirect-detection reagents that were evaluated was adjusted to give a background absorption of *ca.* 0.05 A.U.

A 0.03 mol/l creatinine–acetic acid buffer has been reported for the detection of metal ions [13], but when this was used in these studies (75-μm capillary) the background absorption was out of linearity range, and a relatively small signal-to-noise (*S/N*) ratio of 26 was observed for a $1 \cdot 10^{-4}$ mol/l sample of Ce^{3+}. Creatinine was chosen by Foret *et al.* [13] since its pK_a value of 4.8 permits it to act as a good buffer in the desired working range. However, if the pH is 4.8, only half of the creatinine is in the cationic form. The neutral fraction does not contribute to detection, but does affect the linearity range. Therefore, aromatic amines with pK_a values larger than 7 or quaternary ammonium salts should offer advantages for indirect detection. Since the pK_a of aromatic amines with an amino group connected to a benzene ring is around 4, aromatic

TABLE I

MOLAR ABSORBANCE OF INDIRECT-DETECTION REAGENTS AT 214 nm IN A pH 4.6 SOLUTION

Compound	Molar absorbance (cm^{-1} mol^{-1} l)
Creatinine	$9.2 \cdot 10^3$
Benzylamine	$4.3 \cdot 10^3$
N-Methylbenzylamine	$4.8 \cdot 10^3$
N-1-Naphthylethylenediamine dihydrochloride	$4.8 \cdot 10^4$
Benzyltrimethylammonium chloride	$1.3 \cdot 10^4$
N,N-Dimethylbenzylamine	$6.0 \cdot 10^3$
Naphthene methylamine	$4.4 \cdot 10^4$

amines with the amino group connected via an alkyl group (larger pK_a) are preferred. In this study seven different aromatic amines and quaternary ammonium salts were selected based on their acid/base properties and their molar absorbance values (see Table I).

With benzylamine (electrolyte contained 4 mmol/l HIBA, 9 mmol/l benzylamine and acetic acid at pH 4.6) it was possible to detect all 14 lanthanides, but the S/N was only 22 for a sample containing $1 \cdot 10^{-4}$ mol/l Ce^{3+}. It was found that N-methylbenzylamine also gave good detection, but the improvement in S/N was very small. Both benzyltrimethylammonium chloride and N-1-naphthylethylenediamine dihydrogenchloride gave complex electropherograms in which several positive peaks appeared before a series negative peaks when a mixture of 14 lanthanides were injected. When individual lanthanide samples (La^{3+}, Ce^{3+} and Pr^{3+}) were injected separately, both a positive and a negative peak were obtained for each ion, as shown in Fig. 1. This phenomena appeared to be related to the presence of Na^+, which was added as NaOH to adjust the pH of these electrolytes. The change in concentration of Na^+ when the sample is introduced should cause a positive peak, but the reason for its appearance at a different retention time for different metal ions is unclear. Because of these interferences, however, these two reagents were not studied further.

Table I shows that the molar absorbance of naphthenemethylamine is relatively large, and thus should give sensitive detection. Unfortunately this reagent was not stable. After distillation under vacuum, it became pale yellow within a few hours when stored under nitorgen. In an effort to stabilize this compound an acetate salt was prepared and recrystallized three times from methanol–diethyl ether. To maintain the detector reading within the linear range, the concentration of the acetate salt could not be more than 2 mmol/l. However, the pH of solution containing 4.2 mmol/l HIBA and 2 mmol/l salt was 2.8. At this pH value, the baseline noise was high, the S/N was less than 4 and, because of a fast electroosmotic flow (EOF), the separation was poor. Lower concentrations of HIBA could be used to adjust the pH, but this would also degrade the separation.

The best indirect reagent was DBA. This reagent gave S/N values of >100 for a $1 \cdot 10^{-4}$ mol/l Ce^{3+} solution. Detection limits obtained with DBA are given later in this report.

Capillary internal diameter

In principle higher heat dissipation is obtained with smaller-diameter capillaries, and higher column efficiencies should be obtained with smaller capillaries. However, as the ionic strength of the buffer used in these studies was only 6 mmol/l, the current was about 8 μA with 75-μm capillaries, and

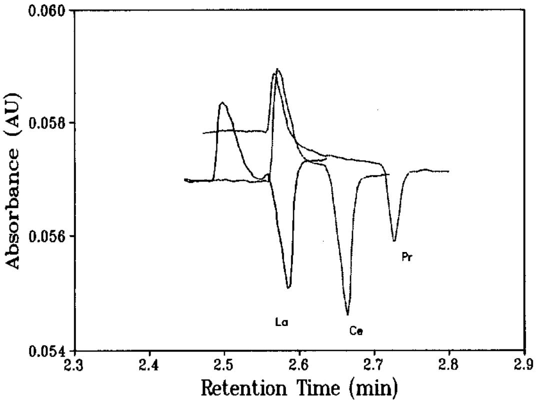

Fig. 1. Electropherogram of La^{3+}, Ce^{3+} and Pr^{3+} on an unbonded capillary. Each sample was injected separately. Electrolyte, 8 mmol/l benzyltrimethylammonium chloride and 4 mmol/l HIBA at pH 4.6 adjusted with sodium hydroxide; capillary, 60 cm × 75 μm fused-silica; electric field, 500 V/cm; injection, 6 s at a differential height of 9.8 cm; indirect detection at 214 nm; concentration of ions, $1 \cdot 10^{-4}$ mol/l.

heat dissipation was not a problem for most of the experimental conditions studied. The results in Table II show that when 25-μm, 50-μm and 75-μm unbonded capillaries were evaluated the 75-μm capillary give the highest *S*/*N* value and a low HETP (height equivalent to a theoretical plate) value. With smaller capillaries it is possible to work with higher concentrations of the indirect-detection reagent, which should extend the upper part of the linear working range, but the alignment of the smaller capillaries in the instrument was more difficult. Consequently, 75-μm capillaries were used for the remainder of these studies.

Effect of pH

In the separation of ions the net mobility of an ion is the summation of EOF and electrophoretic mobility. In these studies a weak complexing agent is used to enhance differences in the electrophoretic mobilities, which is the weighted average of the mobility of the free metal ions and its various complexes. Since both the EOF [23] and the speciation of the metal ions is influenced by pH; the pH range from 3.3 to 5.3 (pK_a of HIBA = 3.79 [24]) was studied on unbonded and C_1 and C_{18} bonded-phase capillaries. The *S*/*N* ratios and HETP values for Ce^{3+} ($1 \cdot 10^{-4}$ mol/l) at diferent pH values are shown in Table III. The results in Table III show that the *S*/*N* values decrease as the pH decreased. This was caused by an increase in the baseline noise which may have been caused by excessive heating due to an increase in the current as a result of the greater mobility of the hydronium ions. At the highest pH value, 5.3, the peaks of lanthanide ions began to broaden on both the unbonded and C_1 capillaries, possibly due to interactions between the cations and the silica surface. The results in Fig. 2 show that the electrophoretic coefficients of the ions decreased as the pH was increased due to complexation. Based on the data shown in Table III and Fig. 2, a pH of 5.0 was chosen to optimize both *S*/*N*, HETP values and resolution.

Effect of HIBA concentration

Metal ions belonging to groups such as the transition and lanthanide groups have similar electrophoretic mobilities, and to achieve efficient separations it is necessary to selectively alter the mobilities via some process such as complexation. Complexation reagents such as cyanide [11], 8-hydroxyquinoline-5-sulfonic acid [14], pyridylazoresorcinol [10] and HIBA [13,18–21] have been used. Since HIBA is known to be effective for the selective separation of lanthanides this reagent was chosen for these studies. The net electrophoretic mobility of metal

TABLE II

S/*N* RATIO AND HETP OF Ce(III) FOR DIFFERENT CAPILLARIES

Electrolyte, 6 mmol/l DBA and 4 mmol/l HIBA; the pH (4.6) was adjusted with acetic acid; Ce^{3+} concentration, $1 \cdot 10^{-4}$ mol/l.

Size of capillary (μm)	*S*/*N*	HETP (μm)
75	60	3.2
50	26	3.5
25	3.6	6.4

TABLE III

S/*N* AND HETP FOR Ce(III) AS A FUNCTION OF pH

Electrolyte, 6 mmol/l DBA and 4 mmol/l HIBA; the pH was adjusted with acetic acid; Ce^{3+} concentration, $1 \cdot 10^{-4}$ mol/l.

pH	Capillary	*S*/*N*	HETP (μm)
5.3	Unbonded	65	20
	C_1	30	27
	C_{18}	50	2.6
4.95	Unbonded	105	2.3
	C_1	65	2.7
	C_{18}	105	3.2
4.8	Unbonded	85	2.1
	C_1	82	2.6
	C_{18}	85	2.7
4.3	Unbonded	70	2.5
	C_1	60	3.6
	C_{18}	60	2.6
4.0	Unbonded	40	3.5
	C_1	40	3.8
	C_{18}	60	3.6
3.8	Unbonded	50	4.8
	C_1	20	4.6
	C_{18}	65	4.6
3.3	C_{18}	4	–

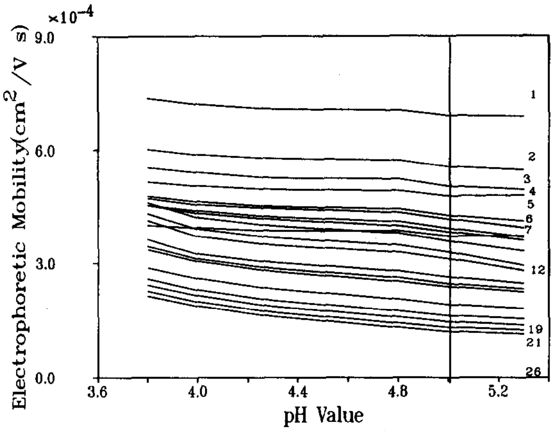

Fig. 2. Electrophoretic coefficients as a function of pH. Electrolyte, 6 mmol/l DBA and 4 mmol/l HIBA, pH adjusted with acetic acid; other conditions as for Fig. 1. Solute identity: 1 = K^+; 2 = Ba^{2+}; 3 = Ca^{2+}; 4 = Na^+; 5 = Mg^{2+}; 6 = Mn^{2+}; 7 = Fe^{2+}; 8 = Co^{2+}; 9 = Ni^{2+}; 10 = Zn^{2+}; 11 = Li^+; 12 = La^{3+}; 13 = Ce^{3+}; 14 = Pr^{3+}; 15 = Nd^{3+}; 16 = Sm^{3+}; 17 = Eu^{3+}; 18 = Gd^{3+}; 19 = Cu^{2+}; 20 = Tb^{3+}; 21 = Dy^{3+}; 22 = Ho^{3+}; 23 = Er^{3+}; 24 = Tm^{3+}; 25 = Yb^{3+}; 26 = Lu^{3+}.

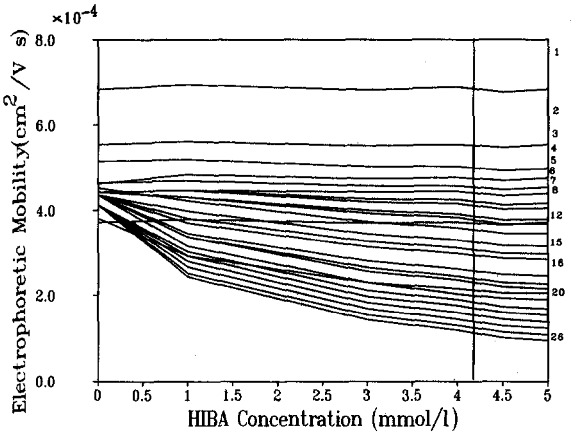

Fig. 3. Electrophoretic coefficients as a function of the concentration of HIBA. Electrolyte, 6 mmol/l DBA at pH 5.0 adjusted with acetic acid; solute identity as for Fig. 2; other conditions as for Fig. 1.

ions is dependent on the degree of complex formation, and thus the separation of the ions is influenced by the concentration of HIBA. Therefore, the concentration of HIBA was studied over the range 0–5 mmol/l at pH 5.0 with an electrolyte containing 6 mmol/l DBA; to maintain the previously determined optimum pH of 5, 5 mmol/l was the upper HIBA concentration that could be used with 6 mmol/l DBA. The electrophoretic coefficients of each ion as a function of the concentration of HIBA are shown in Fig. 3. In the absence of HIBA only group separations were possible. The results in Fig. 3 show that the best separation of the 26 metal ions was obtained when the concentration of HIBA was 4.2 mmol/l, which is in close agreement with similar studies reported previously [18].

Effect of the surfactants

The EOF in bonded-phase and unbonded capillaries can be manipulated by adding small amounts of surfactants [19]. Non-ionic surfactants reduce the EOF to *ca.* 0 and cationic surfactants can both reduce and reverse the EOF. Manipulation of the EOF can be used to optimize resolution as long as column efficiency is not degraded. Consequently, the influence of TX-100 and CTAC was examined. The column efficiencies and retention times observed for Ce^{3+} on bonded-phase and unbonded capillaries when surfactants were added are shown in Table IV. Good separations were obtained when TX-100 was added, but broad peaks were found with CTAC, except at higher concentrations; the broad peaks may be a result of interactions between the hydrophobic chain of CTAC and the HIBA–metal complexes. Overall, there were only small differences between the performance of the bonded-phase and unbonded capillaries, and the best combination of column efficiency and resolution was obtained when a 0.2 mmol/l solution of TX-100 was used. As expected from EOF effects, the migration times of Ce^{3+} increased with the concentration of TX-100 and reversed with higher concentrations of CTAC. Fig. 4 shows an example of the separation obtained under these optimum conditions; note that the peaks in Fig. 4 are negative due to indirect detection, but could easily be made positive by reversing the polarity of the detector output. The HETP values for the metal ion shown in Fig. 5 were in the range 1–10 μm. The minimum values were observed for Ce^{3+} and Pr^{3+}, which had a mobility that matched that of the electrolyte cation; metal ions with higher mobilities exhibited tailing peaks and slower migrating ion exhibited fronting peaks.

The values of EOF flow for unbonded, C_1 and C_{18} phases with 0.2 mmol/l TX-100 in the electro-

TABLE IV

HETP OF Ce(III) AS A FUNCTION OF SURFACTANT CONCENTRATION

Electrolyte, 6 mmol/l DBA and 4 mmol/l HIBA; the pH was adjusted with acetic acid; Ce^{3+} concentration, $1 \cdot 10^{-4}$ mol/l.

Surfactant	Concentration (mmol/l)	Capillary	HETP (μm)	t_R (min)
TX-100	0.02	Unbonded	2.1	2.50
		C_1	2.9	2.67
		C_{18}	2.2	2.85
	0.05	Unbonded	1.9	2.92
		C_1	2.4	2.81
		C_{18}	2.3	2.90
	0.10	Unbonded	7.9	3.16
		C_1	2.8	3.27
		C_{18}	3.6	2.99
	0.20	Unbonded	1.2	4.33
		C_1	1.4	4.14
		C_{18}	2.0	3.17
CTAC	0.01	Unbonded	4.1	2.49
		C_1	3.7	1.67
		C_{18}	7.7	2.29
	0.05	Unbonded	7.8	2.73
		C_1	7.8	2.08
		C_{18}	20	2.64
	0.20	Unbonded	–	7.40
		C_1	5.2	−4.20[a]
		C_{18}	16	−4.75
	0.40	Unbonded	3.9	−3.77
		C_1	3.2	−2.37
		C_{18}	6.5	−2.61

[a] A negative retention time indicates a reversal in flow.

lyte were $6.0 \cdot 10^{-5}$, $6.8 \cdot 10^{-5}$ and $1.2 \cdot 10^{-4}$ cm^2 V^{-1} s^{-1}, respectively. These results suggest that TX-100 was absorbed more readily on the unbonded capillary surface. The unbonded capillary also gave a higher column efficiency than C_{18} capillaries, possibly due to reduced interactions between the surface and the solute. The HETP values obtained in these studies are a factor of at least 2 better than those reported for a polyamide-coated capillary [13].

Analytical performance parameters

Detection limits ($S/N = 3$) were *ca.* 1 μg/ml for the lanthanides, *ca.* 0.6 μg/ml for transition and alkaline earth ions and *ca.* 0.1–0.8 μg/ml for alkali metal ions. Relative standard deviations of the areas (four measurements) obtained for each of the lanthanides were determined for the electrolyte not containing a surfactant. The averages (standard deviation given in parentheses) of the relative standard deviations were 3.7 (1.1%), 5.1 (2.2%) and 2.5 (1.1%) on unbonded, C_1 and C_{18} capillaries, respectively. The linearity of the calibration curve was evaluated for the range $1 \cdot 10^{-5}$ to $4 \cdot 10^{-4}$ mol/l for each metal ion; the maximum concentration was chosen to give a concentration that was 100 times less than the concentration of buffer to minimize peak broadening due to differences between the

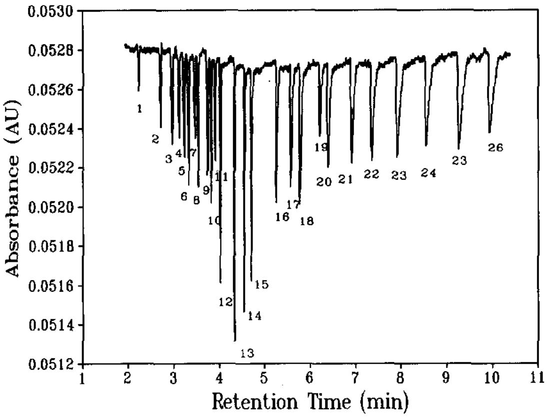

Fig. 4. Electropherogram for the separation 26 metal ions on an unbonded capillary. Electrolyte, 6 mmol/l DBA and 4.2 mmol/l HIBA at pH 5.0 adjusted with acetic acid and 0.2 mmol/l TX-100; peak identity as for Fig. 2; other conditions as Fig. 1.

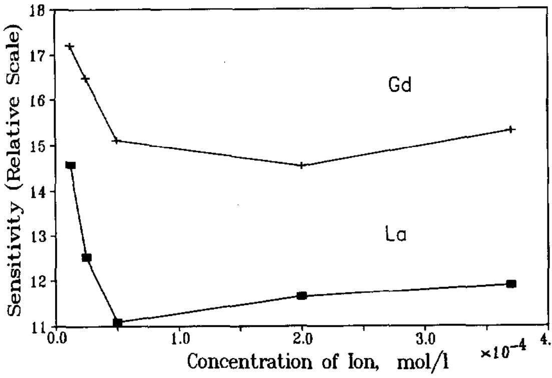

Fig. 5. Corrected sensitivity plots for Gd^{3+} and La^{3+}. Conditions as for Fig. 4 without TX-100.

electrolytes and analyte mobilities [25]. Conventional calibration curves were visually linear over the entire range; regression analysis for two of the test metal ions, La and Gd, gave values of 1.000 for the coefficients of determination (r^2) and the standard error of the slope was *ca.* 1%. However, when the sensitivity values for these two metal ions are corrected for the *y*-axis intercept and plotted *versus* concentration it is obvious that the curves are not linear in the low concentration range (see Fig. 5); perfectly linear data would give a straight-line sensitivity plot with a slope of zero. When the lowest concentration points in Fig. 5 are omitted, the remaining data for La and Gd give average sensitivity values of 11.8 and 15.5, and all of these data points lie within a linearity range of ±6%. Problem associated with the application of conventional regression analysis to the determination of the linearity calibration curves have been discussed in more detail elsewhere [26].

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the Natural Science and Engineering Research Council of Canada and Waters/ Millipore.

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